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13. ABSTRACT ***(Maximum 200 words)***

Molybdenum nitride (Mo_xN (x=1 or 2)) films, 15 µm thick, have been deposited via chemical vapor deposition (CVD) on 50 µm thick polycrystalline titanium substrates using molybdenum pentachloride ($MoCl_5$) and NH_3 in a cold wall reactor with vertical pancake heaters. The surface morphology of the films was slightly porous but did not contain the large cracks typical of high surface area Mo_xN films prepared by conversion of MoO_3. Debye-Scherrer calculations indicate that the average particle size of the films was approximately 50 nm. The CVD Mo_xN films had a two-phase structure which appeared to be 60% d-MoN and 40% g-Mo_2N. Energy dispersive X-ray (EDX) data did not reveal the presence of oxygen and chlorine in films deposited above 600°C. Electrode evaluation via AC impedance spectroscopy and cyclic voltammetry indicates that CVD films were capacitive with a voltage stability of 0.9 volts in 6.4 M KOH.

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Characteristics of Molybdenum Nitride Electrodes Grown Via Chemical Vapor Deposition

Molybdenum nitride (Mo_xN (x=1 or 2)) films, 15 µm thick, have been deposited via chemical vapor deposition (CVD) on 50 µm thick polycrystalline titanium substrates using molybdenum pentachloride ($MoCl_5$) and NH_3 in a cold wall reactor with vertical pancake heaters. The surface morphology of the films was slightly porous but did not contain the large cracks typical of high surface area Mo_xN films prepared by conversion of MoO_3. Debye-Scherrer calculations indicate that the average particle size of the films was approximately 50 nm. The CVD Mo_xN films had a two-phase structure which appeared to be 60% δ–MoN and 40% γ–Mo_2N. Energy dispersive X-ray (EDX) data did not reveal the presence of oxygen and chlorine in films deposited above 600°C. Electrode evaluation via AC impedance spectroscopy and cyclic voltammetry indicates that CVD films were capacitive with a voltage stability of 0.9 volts in 6.4 M KOH.

I. Introduction

The numerous potential applications of conductive high surface area (HSA) materials have prompted research and development into growth of these materials. At present, either HSA graphite powder or ruthenium oxide is generally used as electrode materials for double layer capacitors. However, outgassing of CO in aqueous electrolytes during cyclic charging and discharging limits the use of the former and the latter is uneconomical. Due to these problems, alternative materials are being investigated for use as double layer capacitor electrodes as substitutes for graphite and ruthenium oxide. Alternative candidate materials include the transition metal nitrides M_xN_y (M = Mo, Ti, Ni, V, Cr, or W), which have been shown to have electrical conductivities exceeding 10^4 $ohm^{-1}cm^{-1}$ and good resistance to electrochemical decomposition in aqueous electrolytes [1]. More specifically due to its high electrical conductivity and resistance to electrochemical decomposition, molybdenum nitride is a promising candidate electrode material. However, to form high surface area films (> 30 m^2/g) of molybdenum nitride, it is advantageous to make use of densification via conversion of MoO_3 to molybdenum nitride [2-5]. Within the molybdenum compound family, the bulk density of MoO_3 (ρ = 4.69 g/cm^3) is less than MoN (ρ = 9.05 g/cm^3), and Mo_2N (ρ = 9.50 g/cm^3). In the conversion of MoO^3 to molybdenum nitride, it is evident that the formation Mo^2N or MoN would cause a large increase in surface area (i.e., microcracks, pores, and cavitation) given that the densification is not associated with significant shrinkage of the nitride.

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Upon trying to convert MoO_3 films to Mo_xN some unreacted oxides will remain [6]. Molybdenum dioxide (MoO_2), which is produced in the incomplete conversion of MoO_3 to Mo_xN, has a + 0.676 volt stability in 4.4 M H_2SO_4 electrolyte. Such oxide contaminated Mo_xN electrodes are limited to a 0.70 volt stability in charging and discharging cycles in 4.4 M H_2SO_4 electrolytes. To reduce the oxide contamination in Mo_xN electrodes, a direct growth process (CVD) using $MoCl_5$ and NH_3 has been employed.

II. Experimental Procedures

As-received polycrystalline titanium substrates were cut into 1" squares and degreased in pure trichloroethylene, acetone, and methanol in sequential order. The substrates were then etched in a solution of 1.0 M HCl at 90°C for 10 minutes to remove the oxide scale layer. The etched substrates were rinsed and held in pure methanol prior to deposition.

The etched substrates were placed on a molybdenum holder contained in a cold wall, vertical CVD system. The system was evacuated to 10^{-3} Torr and back-filled with ultra high purity (UHP) N_2 to 1000 Torr. This process was repeated seven times to reduce oxygen present in the system to the amount contained in the UHP N_2. The UHP N_2 was also used as the carrier gas for the $MoCl_5$, which was contained in a stainless steel metalorganic bubbler. The bubbler was maintained at a constant temperature of 55°C to give a $MoCl_5$ vapor pressure of 2 Torr. The $MoCl_5/N_2$ gas delivery line to the deposition region was heated to slightly higher temperatures than the bubbler temperature to reduce condensation of $MoCl_5$. The unheated NH_3 gas delivery line was isolated from the $MoCl_5$ delivery line to minimize the formation of NH_4Cl. The formation of NH_4Cl was also minimized by employing an alternating cycle deposition method, in which $MoCl_5$ was cycled for 0.5 seconds every minute, while NH_3 flow was maintained at all times except when the $MoCl_5/N_2$ was flowing. The $MoCl_5/N_2$ and NH_3 flow rates during the deposition process were 2.5 l/min and 1.5 l/min respectively, and were controlled by mass flow controllers. The deposition pressure was 100 Torr and was maintained by a throttle valve. The substrates were heated by a resistive SiC-coated graphite heater to the desired Mo_xN deposition temperature, and the deposition cycle was initiated by flowing $N_2/MoCl_5$ for 0.5 seconds. Termination of the deposition process was accomplished by cessation of the $MoCl_5/N_2$ flow, while maintaining NH_3 flow for 5 minutes at deposition temperatures.

The electrical, structural, and chemical characteristics of the Mo_xN films were analyzed. Scanning electron microscopy (SEM) was performed using a JEOL 6400FE operating at 5 kv which was equipped with an Oxford Light Element Energy Dispersive X-ray (EDX) Microanalyzer. X-ray diffraction (XRD) data was obtained on a Rigaku X-ray diffraction apparatus operating at 27.5 kv. Electrical properties of the Mo_xN electrodes were evaluated by AC impedance spectroscopy and cyclic voltammetry in 6.4M KOH electrolytes.

III. Results and Discussion

The HSA film electrodes currently used in double layer energy storage devices generally have a macroscopic, highly-cracked microstructure. In the present research, polycrystalline Mo_xN films have been deposited on titanium substrates without the mud-crack macrostructure. As shown in Fig. 1a, the thickness across the textured surface of CVD Mo_xN films varied by 1 µm on 15 µm thick films. An SEM micrograph of a Mo_xN electrode prepared by the conversion of MoO_3 is shown for comparison in Fig. 1b. The surface roughness of CVD Mo_xN films is more apparent in 45° rotation SEM micrographs shown in Fig. 2a and Fig. 2b. The surface roughness is believed to be due to a combination of high deposition rates (1 µm/min) and rapid surface reaction of $MoCl_5$ and NH_3. With a deposition rate of 1 µm/min at 600°C, very little surface diffusion occurs and particles remain "frozen" on the surface and react rapidly when exposed to NH_3. Higher deposition rates would be detrimental to film quality, crystallinity, and adhesion.

The chemical properties of the Mo_xN films were examined using XRD and EDX. X-ray diffraction patterns of the two phase CVD and converted Mo_xN films are shown in Fig. 3a and Fig. 3b, respectively. The CVD films consisted of ≈ 60% δ-MoN and 40% γ-Mo_2N; and converted Mo_xN films consisted of ≈ 60% γ-Mo_2N and 40% δ-MoN. The peak broadening in the XRD patterns was due to nanoparticle formation in the films. Furthermore, the EDX pattern, with the nitrogen peak removed for clarity, of a typical CVD Mo_xN film deposited at 600°C indicates that no residual chlorides or oxides were present. However, at deposition temperatures less than 400°C chlorine was detected. This was due to the difficulty in thermally cracking NH_3 at temperatures below 500°C. As shown in Fig. 4b, the EDX pattern for a typical Mo_xN film prepared by the conversion of MoO_3 shows considerable amounts of oxygen present in the film. The oxygen present in the CVD Mo_xN films approximates the amount of residual oxygen present due to physical absorption of water, air, and hydrocarbons on the surface of the film.

The Debye-Scherrer equation (Eq. 1) was used to calculate the average particle size of the films using the XRD patterns,

$$d=K\lambda/\beta_{hkl}\cos\theta. \qquad (1)$$

Theta (θ) is the Bragg angle; λ is the X-ray wavelength; β_{hkl} is the peak width at half maximum peak height, corrected for instrument broadening; and the correction factor K was taken as unity. To minimize the effects of peak broadening due to residual stresses, particle size calculations were conducted using peak values less than 20°. As shown in Table I, the average particle size of the CVD Mo_xN films was 53 nm, where as the average particle size of converted Mo_xN films was 10 nm.

(a) (b)

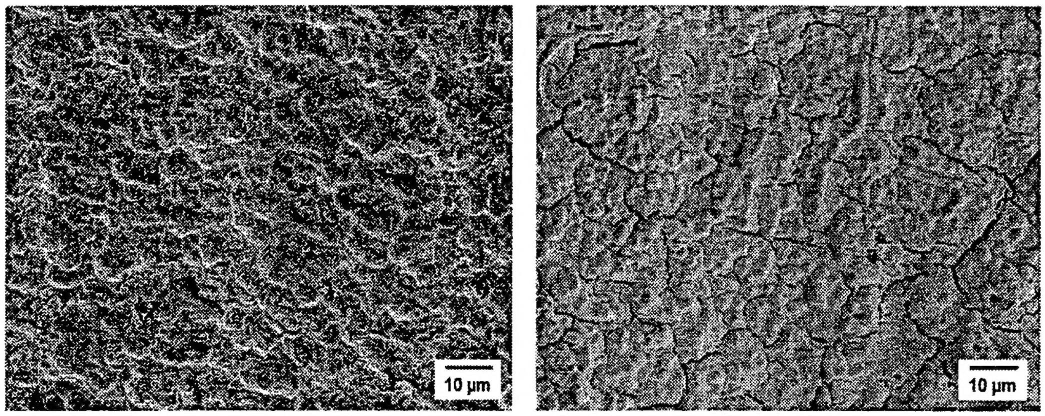

Figure 1. SEM micrographs of (a) CVD Mo_xN film and (b) Mo_xN film converted from MoO_3. The surface of the CVD film does not have the mud crack structure present in (b).

(a) (b)

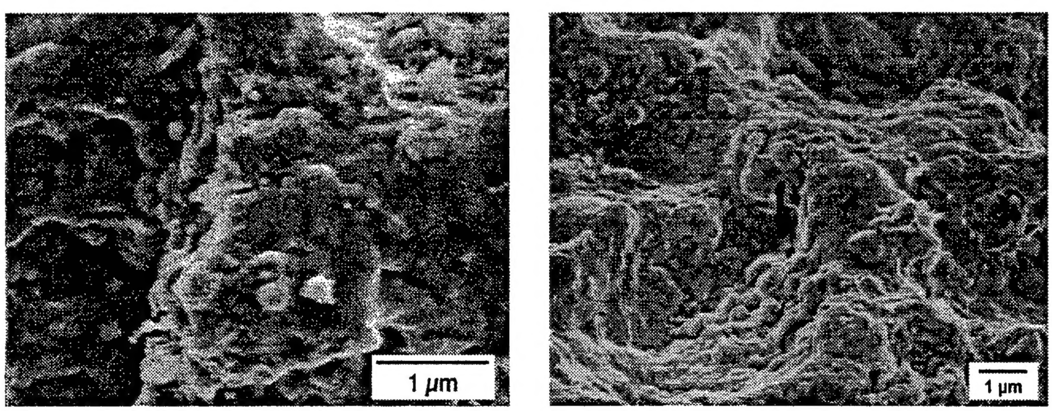

Figure 2. Scanning electron micrographs of CVD Mo_xN films at 45° rotation at (a) magnification of 25,000 and (b) magnification of 10,000. Note the variation in film thickness and the roughness of the surface.

Surface area generation in the conversion of MoO_3 to Mo_xN is the result of the densification of MoO_3 to Mo_2N without the collapse of individual particles. This is called "topotactic" because the crystallographic direction relationships between MoO_3 and Mo_2N are retained [5]. The topotactic reaction creates surface area by the generation of pores in Mo_2N without the collapse of individual crystals. For CVD Mo_xN films, surface area generation takes place by a different process. Molybdenum pentachloride (trigonal, ρ = 2.98 g/cm^3) reacts rapidly with NH_3 at elevated temperatures to produce Mo_xN (ρ = 9.05 g/cm^3). This change in density, can create adherence problems. However, the

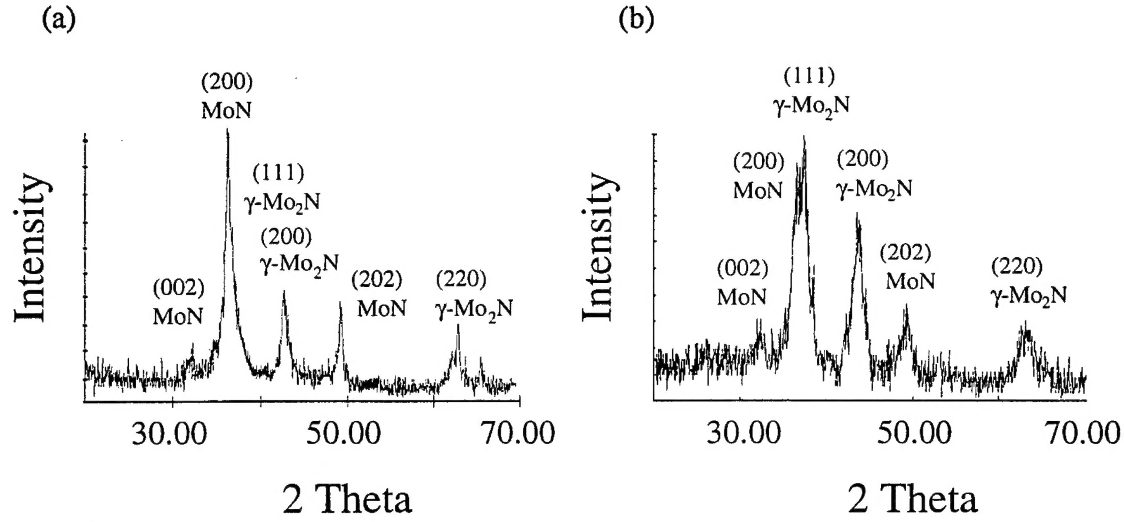

Figure 3. X-ray diffraction patterns of (a) CVD Mo_xN film and (b) Mo_xN film converted from MoO_3. The peak broadening in (a) and (b) is due to nanoparticle formation.

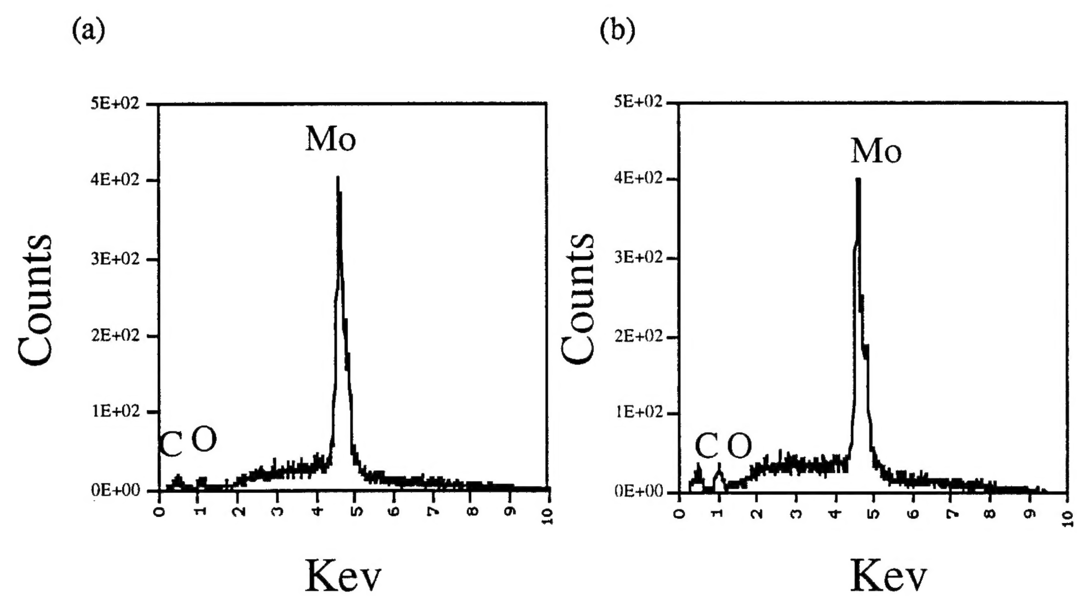

Figure 4. Energy dispersive X-ray patterns of (a) CVD Mo_xN film and (b) Mo_xN film converted from MoO_3. Oxygen contamination was observed in (b).

rapid reaction of $MoCl_5$ and NH_3 can produce a porous structure without sacrificing film adherence if the deposition reaction is optimized. If the deposition rate is too slow, the complete densification of $MoCl_5$ will occur which can reduce the surface area. However, if the deposition rate is optimal, then the densification of $MoCl_5$ to Mo_xN occurs rapidly to

Table I. Calculated Average Particle Sizes of Mo_xN Films Produced by CVD and Conversion Form MoO_3

Process	Phase	θ	Cos θ	β_{hkl}	Particle Size
CVD	MoN	15.944	0.9615	0.0030	53.31 nm
CVD	MoN	18.103	0.9504	0.0030	54.09 nm
CVD	Mo_2N	18.688	0.9472	0.0031	51.72 nm
Conversion	MoN	15.944	0.9615	0.0147	10.47 nm
Conversion	MoN	18.103	0.9504	0.0149	10.33 nm
Conversion	Mo_2N	18.688	0.9472	0.0151	10.19 nm

produce pores in the bulk of the structure, while remaining adhered to the substrate. As shown in Fig. 5a, the increase in deposition rate produced an increase in the surface area of the films. This is a direct result of the rapid reaction of $MoCl_5$ and NH_3. The surface area was also discovered to increase with the deposition temperature, as shown in Fig. 5b. This was due to the complete conversion of $MoCl_5$ to Mo_xN and subsequent production of pores in the film.

Molybdenum nitride electrodes were evaluated in 6.4M KOH electrolytes by AC impedance spectroscopy and cyclic voltammetry to determine their capacitance and electrochemical stability. In Fig. 6, the slope of the line in plots of frequency versus impedance is -1 which is typical of ideal porous electrodes displaying double layer capacitance. In Fig. 7, a cyclic voltammogram of a representative CVD Mo_xN electrode in the 6.4M KOH electrolyte is shown. The capacitance was determined to be 0.30 F/cm^2, which is less than Mo_xN electrodes prepared by conversion of MoO_3. However, the voltage stability of CVD Mo_xN electrodes is 0.9 volts which is 0.2 volts higher than Mo_xN electrodes prepared by the conversion of MoO_3.

IV. Conclusions

Mo_xN (MoN 60% and Mo_2N 40%) films void of large cracks on the surface have been deposited via CVD on polycrystalline titanium substrates. The EDX data shows a significant reduction in oxygen contamination in Mo_xN CVD films when compared to Mo_xN films prepared by the conversion of MoO_3. The average particle size of the CVD films was determined by Debye-Scherrer calculations to be ≈ 50 nm. The two phase Mo_xN films consisted of ≈ 60% MoN and 40% γ-Mo_2N. AC Impedance and cyclic voltammetry data indicate that CVD Mo_xN films are capacitive with voltage stability of 0.9 volts in 6.4 M KOH electrolytes.

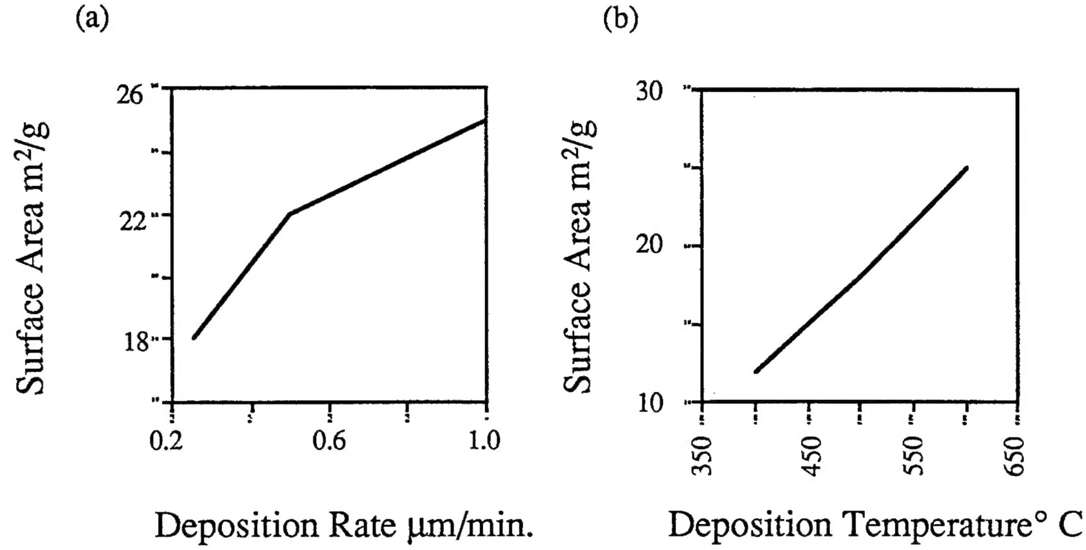

Figure 5. Plots of the surface area of CVD Mo_xN films versus (a) deposition rate at 600°C and (b) deposition temperature. The surface area was found to increase with both increasing deposition temperature and deposition rate.

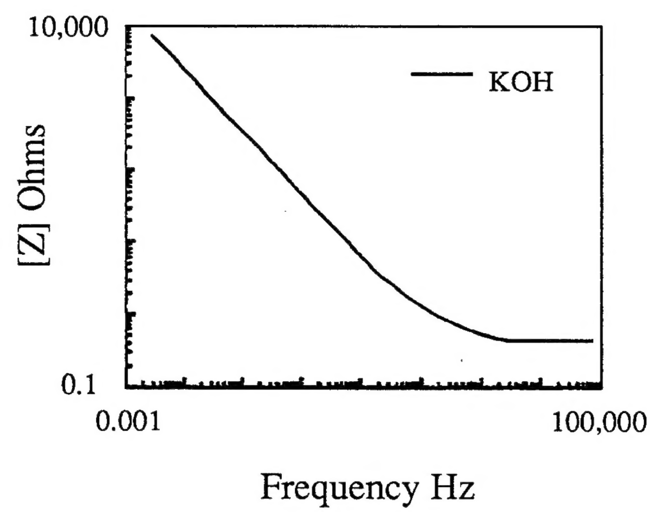

Figure 6. An AC impedance spectroscopy plot of frequency versus impedance. The slope of the line indicates a capacitive response of the electrode.

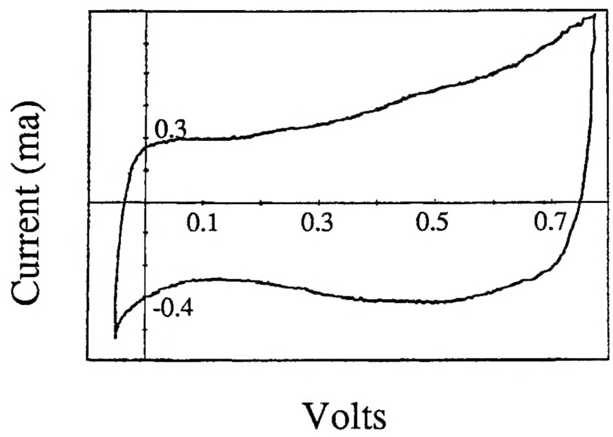

Figure 7. Cyclic voltammogram of CVD Mo_xN electrode in 6.4 M KOH.

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